POLYMER SCIENCE DICTIONARY

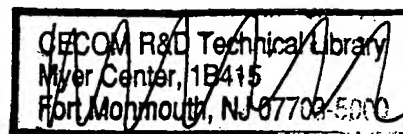## MARK S. M. ALGER

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network form. Aminoresins are important commercial polymers, being widely used as thermosetting plastic moulding and laminating resins, in coatings and varnishes and as textile (especially cotton textile) finishes. The most important types are urea–formaldehyde and melamine–formaldehyde polymers. Of lesser importance are benzo-guanamine—formaldehyde, aniline–formaldehyde and other urea–formaldehyde resins such as thiourea, cyclic ureas, e.g. ethyleneurea, and dicyanamide–formaldehyde resins. The initially formed polymers are often condensed methylol derivatives of the amines or amides with methylene bridges (in urea–formaldehydes) and/or ether methylene bridges, as in melamine–formaldehydes. The prepolymer, after fabrication, may then be crosslinked to form a network thermoset plastic product.

AMINOSILANE A silane coupling agent containing amino groups. Examples include γ-aminopropyltri-methoxysilane and N-β-(aminoethyl)-γ-aminopropyl-trimethoxysilane.

AMINOSUGAR A monosaccharide (or sugar) or monosaccharide unit in which a hydroxyl group has been replaced by an amino group or by an N-acetyl-amino group (—$NHCOCH_3$). In their nomenclature the amino-sugars are formally regarded as being formed via the deoxysugar. Thus common naturally occurring examples (mostly in animals and micro-organisms) are D-glucos-amine (or 2-deoxy-2-amino-D-glucose), D-galactosamine (or 2-deoxy-2-amino-D-galactose) and its acetylated derivative sialic acid.

11-(or ω-)AMINOUNDECANOIC ACID Alternative name for 11-aminoundecylenic acid.

11-(or ω-)AMINOUNDECYLENIC ACID (11-(or ω-) Aminoundecanoic acid)

$$H_2N(CH_2)_{10}COOH \quad M.p.\ 187-191°C.$$

The monomer for nylon 11. Obtained from castor oil, by methanolysis to methyl ricinoleate, which is pyrolysed to methyl undecylenate; the hydrolysed ester is converted to 11-bromoundecylenic acid, which is finally reacted with ammonia to give the desired monomer. Polymerised to nylon 11 (together with about 0·5% lactam in equilib-rium) by heating at about 215°C.

AMMONIA CELLULOSE Alternative name for cel-lulose III.

AMORPHOUS DEFECT A disordered region either within, or on, the surface of a crystal; of no specified structure, but intermediate between the well-defined line, e.g. dislocation, or point defects and the amorphous phase structure. Postulated in order to account for the large loss in crystallinity on introduction of small amounts of comonomer (or other structural impurity) into the polymer chains.

AMORPHOUS ORIENTATION The component of the overall orientation due to the amorphous regions in a polymer. There will similarly be an amorphous compo-nent to each anisotropic property, e.g. birefringence. The amorphous orientation function may be determined by infrared dichroism, laser-Raman scattering or dye-doped polarised fluorescence.

AMORPHOUS POLYMER A polymer in which the molecular chains exist in the random coil conformation; since there is no regularity of structure, there is no crystallinity. Some polymers which are nominally amor-phous may have some short-range order. Use of the term often implies that the polymer is amorphous in the solid state, since polymers are usually amorphous in solution or melt. An irregular conformation is adopted if the molecular structure of the polymer is irregular. Thus atactic polymers, random copolymers and thermoset polymers cannot crystallise due to molecular irregularity, and hence are amorphous. Even regular polymers, which normally crystallise, may often be quenched from the melt state to the amorphous state. Amorphous polymers exhibit a strong T_g, often with additional lower tempera-ture, but weaker, transitions. If non-crosslinked, they are more readily soluble than crystalline polymers. They are normally isotropic (unless oriented) and homogeneous. Since they do not contain crystals to scatter light they are also transparent.

AMORPHOUS REGION A region in a crystalline polymer sample which has not crystallised and therefore in which the polymer chains exist in the random coil conformation, i.e. where the polymer is amorphous. Since crystallisation is limited in a crystalline polymer, amorphous regions are always present, typically account-ing for 10–70% of the material. Thus the whole sample behaves as a 'composite' of amorphous and crystalline polymer. Both regions contribute their characteristic properties to the overall behaviour, with the amorphous regions exhibiting a T_g.

AMORPHOUS SCATTER The X-ray scattering pro-duced by an amorphous polymer or region, consisting of a few diffuse halos. Although no short- or long-range order of a crystalline kind exists, a short-range order of the most probable distances between neighbouring atoms does exist. This is often expressed in terms of the atomic radial distribution function, obtained from the experimental scattering curve.

AMOSITE A fibrous, amphibole asbestos of structure $MgFe_6[(OH)Si_4O_{11}]_2$ (similar to crocidolite), containing a higher proportion of iron than anthophyllite. Forms fibres with a tensile strength of about 2 GPa and a tensile modulus of about 150 GPa, typically 60–100 nm wide and with good acid resistance. Sometimes used as a filler in polypropylene.

AMPHIBOLE A naturally occurring crystalline sili-cate with a ladder polymer structure consisting of two linked chains of alternating SiO_4^{4-} tetrahedra. The double chains are bonded to each other through planes of

CRYSTAL BRANCHING Alternative name for branched crystal.

CRYSTAL–CRYSTAL TRANSITION The transformation of one crystal structure of a polymer to a different structure. It usually results from a change in temperature, as a result of different structures being stable at different temperatures. Few examples are known in polymer crystals, but they include poly-(butene-1) and polytetrafluoroethylene.

CRYSTALLINE ORIENTATION The component of the overall orientation due to the crystalline regions of a polymer. Characterised by its orientation function, f_{cryst}, describing orientation of the crystallite axis with reference to some fixed direction, often the direction of deformation (machine direction). The angle between the two is the crystalline orientation angle, and since there are three crystallographic axes there are three such angles (α, β, ε), and therefore three distributions: $f_\alpha = (3\cos^2\alpha - 1)/2$ and similarly f_β and f_ε, any two of which may be independent. It is determined by intensity measurements of the Debye–Scherrer arcs in wide angle X-ray scattering. The separate reflections of each Miller hkl plane give a $\cos^2\phi_{hkl}$ term from which $\cos^2\alpha$, etc. may be calculated.

CRYSTALLINE RELAXATION A relaxation, with its accompanying transition, associated with the crystalline regions, i.e. the lamellae, of a polymer. The most important relaxation, the primary relaxation, is melting. Sometimes, in addition, a crystal–crystal relaxation and transition are observed, as with polyisoprene and polytetrafluoroethylene. Certain secondary transitions are also sometimes observed, such as premelting and even lower transitions. These may be identified with particular molecular processes, especially where considerable morphological information is available, as is the case with polyethylene. Such processes include short-range co-operative chain motions (similar to those found in amorphous regions), motions associated with defects and with chain folds and interlamellar shear.

CRYSTALLINITY The long-range (hundreds of ångströms) regular ordering of atoms or molecules in unit cells on a three-dimensional crystalline lattice. Non-polymeric solids are essentially 100% crystalline, whereas polymers only crystallise if the molecules have regular structures and then only do so to a limited extent. The extent of crystallinity is often called the degree of crystallinity (or merely crystallinity) and is typically 30–80%. The remaining material is randomly disordered (amorphous), the polymer chains being randomly coiled. The degree of crystallinity realisable decreases with increasing structural irregularity (e.g. atacticity, branching) of the polymer and varies with crystallisation conditions. Thus atactic polymers are usually completely amorphous, whereas 100% crystalline single crystals can be grown under certain special conditions. At the molecular level the crystal structure is characterised by wide angle X-ray

diffraction. However, the polymer crystals (or crystallites) are very small and aggregate usually in an ordered fashion to produce different supermolecular morphologies, e.g. fibrils and spherulites. Crystallinity has a profound effect on polymer properties, especially the mechanical properties, since in the crystallites the polymer molecules are more tightly and evenly packed than in amorphous regions and hence intermolecular forces are higher. Thus as degree of crystallinity increases, so do the moduli, stiffness, yield and tensile strengths, hardness, density and softening points.

CRYSTALLISATION The process of formation of crystalline material from a disordered aggregate of molecules. This may result from cooling a melt to below the polymer crystalline melting temperature (T_m) (melt crystallisation) or from cooling or evaporating a solution (solution crystallisation). Polymer melt crystallisation requires considerable supercooling typically about 30 K. As the temperature is reduced the rate reaches a maximum then diminishes as the melt viscosity increases. Eventually the freezing of molecular motions (below the glass transition temperature) prevents any further crystallisation. Rapid quenching of a melt may prevent any crystallisation occurring. The degree of crystallinity achieved thus depends on the cooling conditions. Crystallisation may also be induced in the solid state by orientation or by annealing.

The progress of crystallisation may be followed by dilatometry, microscopic observation of spherulite growth, wide angle X-ray diffraction or differential scanning calorimetry. The rate–time plot is usually S-shaped. Both primary and secondary crystallisation stages may be observed. Analysis of the kinetics of crystallisation often follows an Avrami equation and yields information on the mechanism, especially nucleation. Nucleation is either heterogeneous due to the presence of impurities, of partially ordered polymer or of deliberately added nucleating agents, or it may be homogeneous, which arises from the random aggregation of polymer molecules to form an ordered region which subsequently grows.

CRYSTALLITE The name given to the crystals present in a crystalline polymer, which, in contrast to non-polymer crystals, are so small as to be observable only with an electron microscope. Typical sizes are 10^{-5} to 10^{-6} cm. Invariably they are of lamellar habit (lamellae) which aggregate such that each crystallite is related to its neighbour, e.g. linearly as in fibrils. The earlier fringed micelle model of a partially crystalline polymer was later replaced by the idea of highly disordered crystallites (as in the paracrystalline model). The demonstration of chain folding in polymer single crystals then led to the current view that crystalline polymers consist of aggregated lamellae, whose thickness of about 100 Å (measured by electron diffraction) is much less than the polymer molecular length (thousands of ångströms). The molecules must therefore lie across the thickness of the lamellae and be folded at the surface. The chain folds may